can occur under the following conditions: (1) in narrow tubes — at the anode, as a consequence of the transport of gas to the anode under the influence of electron collisions; (2) in wide tubes with mercury cathodes — at the cathode, as a consequence of cathode evaporation; (3) in cases of extended contact of the pinch with the walls of the tube — at points of contact, as a consequence of the evolution of absorbed gases from the walls. The last case would seem to explain the effect observed in reference 4.

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5

PARAMAGNETIC RESONANCE OF FREE RADICALS IN WEAK FIELDS

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The line shape and line width for paramagnetic absorption in crystalline α, α-diphenyl β-picryl hydrazyl (dpph) have been investigated at weak fields at room temperature. It is found that the line shape is Lorentzian near the maximum. An estimate of the half-width is found to be in good agreement with theory.[1] Asymptotic Curie points are computed for a number of new radicals.

1. In the absence of hyperfine-structure splitting, the paramagnetic resonance absorption line shape in weak fields is determined essentially by molecular interactions in the paramagnetic system.

The effect of the dipole-dipole interaction on the absorption line shape has been investigated by Waller,[2] Broer,[3] and Van Vleck.[4] The latter characterized the line shape by its moments. The second moment is affected mainly by the central portion of the absorption curve. Higher moments are affected chiefly by the nature of the absorption curve far from the maximum, where the experimental errors are particularly large. Hence a comparison of the experimental and theoretical values of the higher moments can be made only on a qualitative basis.

The nature of the interaction can be ascertained from the central part of the absorption curve. An equation for the absorption curve in the region of the maximum, which takes into account the magnetic dipole-dipole interaction and the Coulomb exchange interaction, has been obtained by Anderson and Weiss[5] who showed that in the case of a strong exchange interaction the curve has a Lorentzian shape with a half-width given by a phenomenological constant.

A more complete quantum-mechanical analysis of the line shape has been developed by Kubo and Tomita;[1] in this treatment it is shown that the absorbed energy, as a function of frequency in the region of the absorption maximum, is proportional to the Fourier component of the function $G(t)$ if the radio-frequency magnetic field is linearly polarized. Hence the characteristics of the line are

given by the function:

$$I(\omega) = \frac{1}{2\pi} \int\limits_{-\infty}^{+\infty} G(t) \exp(-i\omega t)\, dt. \qquad (1)$$

In cases of practical importance ($\hbar\omega \ll kT$), $G(t)$ is determined by the symmetric correlation relation

$$G(t) = \langle \hat{M}_x(t)\, \hat{M}_x + \hat{M}_x\, \hat{M}_x(t) \rangle / 2\, \langle M_x^2 \rangle, \qquad (2)$$

where $\hat{M}_x(t)$ is the magnetization operator in the Heisenberg representation:

$$\hat{M}_x(t) = \exp(it\mathcal{H}/\hbar)\, \hat{M}_x \exp(-it\mathcal{H}/\hbar),$$

and $\mathcal{H}$ is the Hamiltonian of the system in the absence of the variable field. When averages are taken in Eq. (2), the density matrix becomes a constant.

The function $G(t)$ is calculated by a perturbation method. If the total Hamiltonian for the system, $\mathcal{H}$, can be divided into an unperturbed part $\mathcal{H}_0$ for which $\hat{M}_x^0(t)$ can be found easily, and the perturbation $\mathcal{H}'$

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}', \qquad (3)$$

$G(t)$ can be written as an expansion in terms of the small parameter which characterizes the perturbation:

$$G(t) = G_0(t) + G_1(t) + G_2(t) + \ldots \qquad (4)$$

2. The sample chosen to investigate resonance absorption was the relatively well-studied stable radical dpph [$(C_6H_5)_2 N - NC_6H_2(NO_2)_3$]. The magnetic susceptibility of a radical is determined by the spin of the unpaired electron in the molecule ($g = 2.0036 + 0.0002$, cf. reference 6), and follows the Curie-Weiss law with a negative asymptotic Curie point $\Theta = -10°K$.[7] From the antiferromagnetic properties of the radical it may be assumed that there is a strong exchange interaction. In this case the unperturbed Hamiltonian $\mathcal{H}_0$ can be given as a sum of two terms $\mathcal{H}_1 + \mathcal{H}_2$ where

$$\mathcal{H}_1 = \hbar\omega_0 \sum_j \hat{s}_{jz} \qquad (\hbar\omega_0 = g\mu_0 H_0) \qquad (5)$$

corresponds to the Zeeman energy in the external magnetic field H_0 while

$$\mathcal{H}_2 = -2 \sum_{i<j} A\,(r_{ij})\,(\hat{s}_j\,\hat{s}_i) \qquad (6)$$

is the Coulomb exchange interaction.

If it is assumed that the perturbation is the magnetic dipole-dipole interaction and that the exchange of energy between the spin system and the lattice can be neglected, in the weak-field case a Lorentzian curve is obtained close to the maxi-

mum (cf. Appendix):

$$I(\omega) = \frac{1}{2\pi} \frac{\Delta\omega}{(\omega - \omega_0)^2 + \Delta\omega^2} \qquad (7)$$

with half-width

$$\Delta\omega = 4.18\omega_{10}^2/\omega_{20}. \qquad (8)$$

For a polycrystalline sample with a simple cubic lattice structure (constant d) and s = $\frac{1}{2}$

$$\omega_{10}^2 = 3.79g^4\mu_0^4\hbar^{-2}d^{-6}; \qquad (9)$$

$$\omega_{20} = 3.65\,|A|\,/\,\hbar, \qquad (10)$$

where the exchange integral A is expressed in terms of Θ and the number of nearest neighbors z:

$$A = k\Theta/2z = k\Theta/12. \qquad (11)$$

Using Eqs. (8) to (11), we can estimate the half-width of the absorption curve which, in the present case, depends on both the dipole-dipole interaction (ω_{10}) and the exchange interaction (ω_{20}).

Thus the role of exchange interactions can be explained by an analysis of the shape of the experimental absorption curve close to the maximum.

3. The shape of the resonance absorption line in dpph was determined by the oscillator reaction method.[8] A block diagram of the system is shown in Fig. 1.
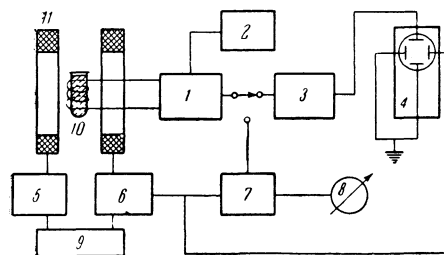
FIG. 1. Block diagram of the system. 1 – oscillator, 2 – heterodyne frequency meter, 3 – broadband amplifier, 4 – oscilloscope, 5 – balanced current-measuring circuit, 6 – modulation source, 7 – narrow-band amplifier, 8 – recorder, 9 – power supply, 10 – sample, 11 – Helmholtz coil.

The sample, containing 250 mg of dpph powder, was placed in the tank circuit of a capacitance-feedback oscillator. The peak grid voltage, at 28 Mcs, was approximately 400 millivolts. The change in oscillator grid voltage at resonance was less than 10 millivolts. Hence a linear relation between the power absorbed in the sample and the oscillator grid voltage may be assumed. The linearity of the system was checked with an auxiliary calibrated tuned circuit which was weakly coupled to the measuring circuit containing the sample being investigated. The power coupled out of the measur-

x*	g-factor	ΔH**, oersteds	Density, g/cm³	Free-radical concentration, percent	d, cm	|Θ|calc, °K	|Θ|exptl, °K
H	2.0042±0.0004	0.85±0.01	1.3	92	8.2	9.4	10
Cl	2.001±0.001	1.0±0.1	1.0	90	9.3	3.8	—
Br	2.002±0.002	1.9±0.1	0.8	92	10.2	1.1	—
OCH₃	2.000±0.002	2.3±0.2	1.1	88	9.0	2.0	—
F	2.000±0.004	3.5±0.4	1.0	89	9.2	1.2	—

*Coefficient in the formula $(x C_6 H_4)(C_6 H_5) N - N C_6 H_2 (NO_2)_3$.

**The value of the width $\Delta H'$, measured at points of maximum slope converted for the half-width of a Lorentzian curve using the formula $\Delta H = \sqrt{3} \; \Delta H'/2$.

ing circuit was determined from the voltage in the calibrated circuit. A linear dependence was found for the entire power range which was investigated.

The absorption lines were observed on an oscilloscope (Fig. 2) after the signal was amplified in a broadband system (30 cps to 1 Mcs) using
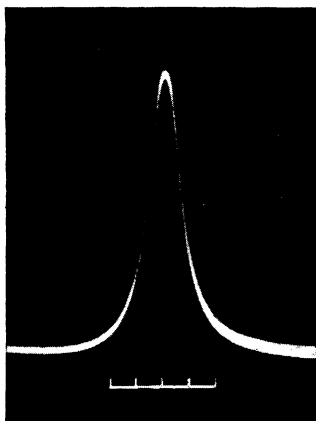

FIG. 2. Oscillogram showing paramagnetic resonance absorption in dpph ($H_0 = 10$ oersteds). The length of the scale corresponds to 4 oersteds.

20-oersted modulation of the fixed field at a frequency of 224 cps. A narrow-band system was used to measure the spacing between points of maximum slope. This system had a bandwidth of 0.3 cps and consisted of an amplifier, synchronous detector, and a recording device. In this work the amplitude of the modulating field was less than 0.1 oersted.

4. To compare the experimental absorption curve (Fig. 2) with a Lorentzian shape, it is convenient to write Eq. (7) in the form:

$$1/I \, (H) = C\Delta H + (C/\Delta H)(H - H_0)^2, \qquad (12)$$

where the constant C is determined by the choice of units. As is apparent from Fig. 3 there is a good fit between the experimental values and a line plotted according to (12).

The experimental value of the half-width of the absorption line for a polycrystalline dpph sample at room temperature and $H = 10$ oersteds ($\omega_0 = 1.76 \times 10^8$ cps) is found to be 0.85 ± 0.01 oersted. This result agrees with values which have been ob-

tained earlier: $(\Delta H = 0.87$ oersted),[7] $(\Delta H = 0.87$ oersted),[9] and $(\Delta H = 0.88$ oersted).[10]
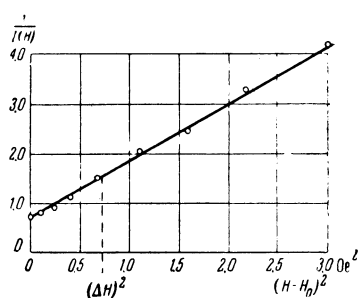

FIG. 3. The points correspond to experimental values measured on the absorption curve. The ordinate scale is arbitrary.

In weak fields, which correspond to resonance frequencies $\omega_0 \ll \omega_{2\gamma} \sim 10^{12}$ cps, it follows from Eqs. (A13) and (A15) of the Appendix that the shape and width of the line are independent of ω_0. Measurements made by us in fields ranging from 2 to 220 oersteds (values of ω_0 ranging from 3.5×10^7 cps to 3.9×10^9 cps) verify this result. In dpph at room temperature, hyperfine-structure splitting has been observed in fields on the order of 8000 oersteds.[11]

For the present sample, a theoretical estimate of the line half-width in a weak field Eq. (8) yields $\Delta H = 0.80$ oersted.

Considering the rough nature of the estimate of the exchange integral and the fact that the actual crystal lattice of the radical differs from a simple cubic structure, the agreement between experiment and theory is quite surprising.

An estimate of the resonance absorption in weak-fields for dpph has been made in reference 12 using the method proposed by Anderson and Weiss.[5] However, because of various errors the calculated width is 35 times greater than the experimental value found by these authors.*

5. The good agreement between theory and experiment in dpph allows us to make an estimate

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*In particular, these authors did not take account of the so-called 10/3 effect, while the estimate of the exchange integral was carried out on the basis of the Curie-Weiss law for ferromagnets.

of the values of the asymptotic Curie points Θ for a number of derivative compounds of dpph; the line shapes for these have been studied by Chirkov and Matevosian.[13]

Using Eqs. (8) to (11) it is easily shown that

$$|\Theta| = 52.3 \, g^4\mu_0^4/k\hbar d^6\Delta\omega. \qquad (13)$$

The calculated and experimental results are shown in the table.

The authors wish to take this opportunity to express their gratitude to G. V. Strotskii for a discussion of this work and for a number of valuable comments and to R. O. Matevosian for making up the samples of the radicals.

APPENDIX

If it is assumed that in the case being considered the perturbation is the magnetic dipole-dipole interaction

$$\mathscr{H}' = \sum_\gamma \mathscr{H}'_\gamma = \sum_\gamma \sum_{jk} \Phi_{jk}^{-\gamma} \{jk\}_\gamma, \qquad (A.1)$$

where

$$\{jk\}_{\pm 2} = \hat{s}_j^\pm \hat{s}_k^\pm, \quad \{jk\}_{\pm 1} = \hat{s}_j^\pm \hat{s}_{kz} + \hat{s}_{jz}\hat{s}_k^\pm,$$

$$\{jk\}_0 = \hat{s}_{jz}\hat{s}_{kz} - \frac{1}{4}(\hat{s}_j^+\hat{s}_k^- + \hat{s}_j^-\hat{s}_k^+), \qquad \hat{s}_j^\pm = \hat{s}_{jx} \pm i\,\hat{s}_{jy}; \qquad (A.2)$$

$$\Phi_{jk}^{\pm 2} = -\sqrt{6\pi/5}\,g^2\mu_0^2 r_{jk}^{-3} Y_{2,\,\pm 2}(\vartheta_{jk}\,\varphi_{jk}),$$

$$\Phi_{jk}^{\pm 1} = -\sqrt{6\pi/5}\,g^2\mu_0^2 r_{jk}^{-3} Y_{2,\,\pm 1}(\vartheta_{jk},\,\varphi_{jk}), \qquad (A.3)$$

$$\Phi_{jk}^0 = -\sqrt{16\pi/5}\,g^2\mu_0^2 r_{jk}^{-3} Y_{2,0}(\vartheta_{jk}\varphi_{jk}),$$

and the $Y_{lm}(\vartheta,\varphi)$ are the normalized spherical functions, we obtain, by carrying out the calculations indicated in (2) to (4),

$$G_0(t) = \frac{1}{2}\exp(i\omega_0 t) + \text{compl. conjug.}, \quad G_1(t) = 0,$$

$$G_2(t) = -\frac{1}{2}\exp(i\omega_0 t)\sum_\gamma \omega_{1\gamma}^2 \int_0^t (t-\tau) \qquad (A.4)$$

$$\times \exp(-i\gamma\omega_0 t)\,f_\gamma(\tau)\,d\tau + \text{compl. conjug.}$$

$$= -\frac{1}{2}\exp(i\omega_0 t)\,\psi(t).$$

Here, in accordance with reference 1, the correlation function $f_\gamma(\tau)$ can be given approximately by the expression:

$$f_\gamma(\tau) = \exp(-\tau^2\omega_{2\gamma}^2/2), \qquad (A.5)$$

where

$$\hbar^2\omega_{2\gamma}^2 = \langle |[\mathscr{H}_2[\hat{M}_x\mathscr{H}'_\gamma]]|^2\rangle / \langle |[\hat{M}_x\mathscr{H}'_\gamma]|^2\rangle. \qquad (A.6)$$

For an isotropic environment

$$\omega_{12}^2 = \omega_{1-1}^2 = \frac{2}{3}\omega_{11}^2 = \frac{2}{3}\omega_{10}^2 = \frac{2}{5}\frac{s(s+1)}{\hbar^2}g^4\mu_0^4\sum_k r_{jk}^{-6}, \qquad (A.7)$$

neglecting higher terms in the expansion in (4), to second order, we may write $G(t)$ in the form

$$G(t) = \frac{1}{2}\exp(i\omega_0 t - \psi(t)) + \text{compl. conjug.} \qquad (A.8)$$

The line shape close to the resonance frequency is determined by the asymptotic behavior of $\psi(t)$ as $t \to \infty$

$$\psi(t) = \sum_\gamma \omega_{1\gamma}^2(|t|\tau'_\gamma - it\tau''_\gamma), \qquad (A.9)$$

where

$$\tau'_\gamma - i\tau''_\gamma = \sqrt{\frac{\pi}{2}}\frac{1}{\omega_{2\gamma}}\exp\left(-\frac{\gamma^2\omega_0^2}{2\omega_{2\gamma}^2}\right)$$

$$\times \left(1 - i\sqrt{\frac{2}{\pi}}\int_0^{\gamma\omega_0/\omega_{2\gamma}}\exp\left(\frac{U^2}{2}\right)dU\right); \qquad (A.10)$$

thus

$$G(t) = \frac{1}{2}\exp\left(i\omega_0 t - \sum_\gamma \omega_{1\gamma}^2(|t|\tau'_\gamma - it\tau''_\gamma)\right)$$

$$+ \text{compl. conjug.} \qquad (A.11)$$

Now it is easy to show, using the results obtained in reference 1, that the line shape close to the maximum is determined by a function of the Lorentzian form:

$$I(\omega) = \frac{1}{2\pi}\frac{\Delta\omega}{(\omega_0 - \omega + \delta)^2 + \Delta\omega^2}. \qquad (A.12)$$

The half-width at half-height is

$$\Delta\omega = \sum_\gamma \omega_{1\gamma}^2\tau'_\gamma = \sum_\gamma \frac{\omega_{1\gamma}^2}{\omega_{2\gamma}}\sqrt{\frac{\pi}{2}}\exp\left(-\frac{\gamma^2\omega_0^2}{2\omega_{2\gamma}^2}\right). \qquad (A.13)$$

In the two limiting cases this expression becomes

$$\omega_0 \to \infty \qquad \Delta\omega_\infty = \frac{\omega_{10}^2}{\omega_{20}}\sqrt{\frac{\pi}{2}}, \qquad (A.14)$$

$$\omega_0 \to 0 \qquad \Delta\omega_0 = \Delta\omega_\infty \sum_\gamma \frac{\omega_{1\gamma}^2}{\omega_{10}^2}\frac{\omega_{20}}{\omega_{2\gamma}}; \qquad (A.15)$$

when $\omega_0 \to 0$ the shift in the resonance peak $\delta = \Sigma\,\omega_{1\gamma}^2\tau''_\gamma$ vanishes.

If $\omega_{20} = \omega_{21} = \omega_{2-1} = \omega_{22}$, we obtain a simple expression for the line width in the weak-field case

$$\Delta\omega_0 = 10\Delta\omega_\infty/3. \qquad (A.16)$$

This is called the $10/3$ effect, due to terms in the perturbation with $\gamma \neq 0$; these are important only at weak fields.

If the crystal has a simple cubic structure with lattice constant d, we get

$$\sum_{k} r_{jk}^{-6} = 8.4 \ d^{-6}, \qquad (A.17)$$

which leads to (9). Assuming that the exchange interaction is isotropic and of the form

$$A(r_{jk}) \begin{array}{ll} = A & r_{jk} < d \\ = 0 & r_{jk} > d \end{array}$$

for a simple cubic lattice and $s = \frac{1}{2}$, as in reference 4, Eq. (A.6) is easily transformed to the expression

$$\omega_{20} = 3.65 \, | \, A \, | \, / \, \hbar. \qquad (A.18)$$

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SECONDARY NUCLEAR REACTIONS INDUCED IN BISMUTH AND LEAD BY HIGH-ENERGY PROTON BOMBARDMENT*

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The production of astatine isotopes (Z = 85) by bombardment of bismuth (Z = 83) and lead (Z = 82) with protons of energies up to 480 Mev was studied radiochemically. The cross sections for At^{211} and At^{210} production from bismuth were found to be 6×10^{-29} and $\sim 2 \times 10^{-29} \, cm^2$ respectively. The formation of the light isotopes At^{205} and At^{203} was established. At^{211} was detected in lead ($\sigma \sim 10^{-31} \, cm^2$).

The experimental results are attributed to secondary capture of the disintegration products (α particles or lithium nuclei). The production of light astatine isotopes is explained by high-energy proton capture with subsequent emission of π^- mesons and several neutrons. The cross section for production of α particles with E > 20 Mev from bismuth irradiated by 480-Mev protons was determined from the astatine yield to be 5 to $6 \times 10^{-25} \, cm^2$.

ONE of the characteristics of interactions between complex nuclei and fast protons is the occurrence of reactions in which the charge of the target nucleus is increased by 2 or 3. Such reactions have frequently been described in the literature[1-3] and are attributed to secondary capture of disintegration products (α particles or lithium nuclei). At high proton energies, in addition to such so-called secondary reactions, there is the additional possibility of proton capture accompanied by the emission of a π^- meson and neutrons, thus also increasing the charge by 2.

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*The experimental work on which this paper is based was performed in 1951 and 1952 (cf. Report of the Institute of Nuclear Problems, Academy of Sciences, U.S.S.R. for 1951).